GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 15, NO. 1, PAGES 3-10, MARCH 2001

Introduction to special section: Ocean measurements and models of carbon sources and sinks

Douglas W.R. Wallace

Forschungsbereich Marine Biogeochemie, Institut für Meereskunde an der Universität Kiel, Kiel, Germany

1. Introduction

This issue of *Global Biogeochemical Cycles* contains a remarkable set of papers, which critically evaluate a variety of model- and observation-based approaches addressing the oceanic distribution, storage, and transport of CO_2. Three of the papers are concerned with observation-based estimates of excess (or anthropogenic) CO_2 [*Coatanoan et al.*, this issue; *Sabine and Feely*, this issue; *Chen*, this issue]. They focus on the approaches, assumptions, and uncertainties involved in detecting the excess CO_2 signal above the ocean's large and variable natural dissolved inorganic carbon (DIC) background. A further paper [*Orr et al.*, this issue] deals with modeling of the uptake of excess CO_2, including a comparison of model results with observation-based estimates. A companion article published in the previous issue of this journal by *Sarmiento et al.* [2000] addresses the preindustrial or "natural" carbon cycle and particularly the role of the ocean in transporting carbon between the Northern and Southern Hemispheres.

2. Storage of Excess CO_2

The term "excess CO_2" refers to carbon inventory or concentration differences within an environmental reservoir (e.g., the ocean, atmosphere, fossil fuel reserves or the terrestrial biosphere) relative to inventories or concentrations that existed during the preindustrial era. Analyses of high-resolution ice cores [*Smith et al.*, 1999; *Indermuehle et al.*, 1999] reveal that atmospheric levels of CO_2 have varied by no more than ~ 20 μatm (1 μatm = 0.101325 Pa) through most of the Holocene. Around the year 1750 atmospheric levels started to rise from the late-Holocene level of ~ 280 μatm, initially owing to excess CO_2 released by land use changes and later owing to fossil fuel combustion. It is generally assumed that prior to 1750 the global carbon cycle was in a steady state that has now been significantly perturbed as a direct result of human activity. Hence the preindustrial era against which excess CO_2 levels are assessed ended around 1750.

In estimating or modeling oceanic levels of excess CO_2, it is almost invariably assumed that changes in the ocean's dissolved carbon content since 1750 have been caused exclusively by an increased net air-to-sea flux driven by the anthropogenic increase of the pCO_2 of the atmosphere. The uptake of excess CO_2 by the oceans during the 1980s was ~2 Pg C yr^{-1} [*Siegenthaler and Sarmiento*, 1993; *Schimel et al.*, 1995] which can be compared with fossil fuel CO_2 releases of ~5.4 Pg C yr^{-1} and an atmospheric inventory increase of ~3.3 Pg C yr^{-1}. The possibility of significant interannual variability in net air-sea fluxes of CO_2 due to other, presumably "natural" causes is currently debated (peak-to-peak amplitude <3 Pg C yr^{-1}: [*Keeling et al.*, 1995; *Francey et al.*, 1995; *Lee et al.*, 1998; *Battle et al.*, 2000]). However, it is generally assumed, but not completely proven, that such short-term, naturally forced, fluctuations average to zero over decadal and longer timescales.

The basic principles that govern the uptake of excess CO_2 by the oceans have been known for at least several decades. The uptake capacity of the ocean for the "extra" CO_2 that has been emitted to the atmosphere is determined by the two following physico-chemical factors: (1) the solubility of CO_2 and the alkalinity of seawater which together determine how much "extra" CO_2 can be stored in the surface ocean in order to regain dynamic equilibrium with an increased atmosphere pCO_2 and, (2) the rate of exposure of deeper, older, ocean waters to this altered atmosphere with increased pCO_2.

The principal issue addressed by global carbon cycle science in the past has been the global budget for excess CO_2 among the three main communicating carbon reservoirs on Earth: the atmosphere, the ocean, and the terrestrial biosphere (including soils). The ocean term in such global budgets has been constrained by a wide variety of approaches, including (1) tracer-calibrated box modeling [e.g., *Oeschger et al.*, 1975; *Siegenthaler and Joos*, 1992]; (2) tracer-validated modeling with general circulation models (GCMs) [e.g. *Maier-Reimer and Hasselmann*, 1987; *Sarmiento et al.*, 1992]; (3) estimates based on *in situ* DIC and $DI^{13}C$ measurements (see papers in this issue plus references therein [*Quay et al.*, 1992]); (4) atmospheric time series of O_2/N_2 [e.g., *Keeling et al.*, 1993; *Keeling et al.*, 1996; *Bender et al.*, 1996] and ^{13}C [e.g. *Ciais*, 1995; *Francey et al.*, 1995]; (5) global integration of net air-sea flux estimates [e.g., *Takahashi et al.*, 1997, 1999]; and (6) atmospheric CO_2 distributions interpreted with atmospheric general circulation models [e.g., *Tans et al.*, 1990].

The papers contained within this issue address approaches 2 [*Orr et al.*, this issue] and 3 [*Chen*, this issue; *Sabine and Feely*, this issue; *Coatanaoan et al.*, this issue]. All the approaches have limitations, potential bias, and error associated with them. Each approach also has its particular set of advantages. However, it appears that we are seeing a remarkable convergence between estimates of global excess CO_2 uptake derived from very different approaches. For example, the results from four separate three-dimensional (3-D) carbon cycle GCMs [*Orr et al.*, this issue] estimate global uptake at 1.85 ± 0.35 Pg C yr^{-1} for the 1980s.

Paper number 2000GB001354.
0886-6236/01/2000GB001354$12.00

Trends in atmospheric O_2/N_2 and CO_2 in the atmosphere over the same period resulted in estimates of ocean uptake of 2.0 ± 0.6 Pg C yr^{-1} [*Langenfelds et al.*, 1999].

3. Ocean and Atmospheric Carbon Transport

Information concerning the locations, magnitudes, and mechanisms of net carbon storage and release in the terrestrial biosphere has proven particularly difficult to obtain. Over the past decade, attention has focused on inferring net fluxes of carbon into and out of the terrestrial biosphere based on inverse modeling of atmospheric CO_2 data. This approach utilizes spatially resolved data on fossil fuel CO_2 releases and atmospheric CO_2 concentrations as constraints within atmospheric transport models. Regional air-sea flux estimates are sometimes applied as an additional constraint. The task is to find a distribution of carbon sources and sinks that when combined with known fossil fuel sources and additional constraints, reproduces the observed spatial distributions of CO_2 (or its stable isotopes) in the atmosphere.

One problem with such an approach is that the atmospheric distribution of CO_2 presently represents a mixture of natural and excess (or anthropogenic) components. Natural gradients of atmospheric pCO_2 exist because both the ocean and atmosphere, as planetary fluids, can transport carbon over large distances between geographically separated natural source and sink regions within the ocean [*Keeling et al.*, 1989; *Broecker and Peng*, 1992]. Natural gradients can also be maintained by covariance of atmospheric (or oceanic) circulation with natural fluctuations in CO_2 concentrations (the "rectifier" effect [e.g., *Pearman and Hyson*, 1981; *Heimann et al.*, 1986; *Keeling et al.*, 1989; *Denning et al.*, 1995]). In the steady state preindustrial carbon cycle, meridional oceanic carbon transport must have been balanced by opposing atmospheric transport. Characterization of the oceanic transport of carbon during the preindustrial era therefore allows the natural component of carbon transport, and hence gradient, within the contemporary atmosphere to be estimated. This in turn can be compared with present-day atmospheric gradients and fossil fuel CO_2 emission patterns in order to infer the location and magnitude of excess CO_2 sinks, both in the ocean and on land. Sarmiento et al. [2000] addressed the preindustrial oceanic transport of carbon with exactly this issue in mind.

4. Current Trends in Carbon Cycle Science

Assuming that the global magnitude of the ocean uptake term in the past is now reasonably well established, attention can turn to the future. It is highly unlikely that the carbon cycle will keep operating in the future as it has in the past [*Tans and Wallace*, 1999]. There is therefore an imperative to monitor the carbon cycle in order to detect changes as they occur and simultaneously to collect information and understanding that can be used to test hypotheses concerning the causes of such changes. For prediction and assessment of the future behavior of terrestrial and oceanic sinks in the context of a changing climate, there is an urgent need for improved process-level understanding. Hence scientific investigation of the global carbon cycle is moving beyond global budgeting issues toward more fundamental and basic issues such as resolving the key processes responsible for present-day oceanic and terrestrial sinks. Process-level understanding concerning which factors control excess CO_2 sinks will be contingent on knowing initially where, geographically, the important sinks are operating. This is presently being addressed by atmospheric inverse modeling [e.g. *Tans et al.*, 1990; *Rayner et al.*, 1999; *Keeling et al.*, 1989; *Enting et al.*, 1995; *Fan et al.*, 1998]. On land, local micrometeorological flux studies combined with climatic, plant physiological, ecological, and soil data can be used to gain insight into mechanisms operating in such regions. In the ocean, time series studies can provide a wealth of information concerning the physical and biogeochemical processes driving carbon fluxes. Improved understanding of where and how water from the deep interior returns to the sea surface is required to better characterize and model excess CO_2 uptake.

A further fundamental question concerns how carbon sinks (and sources) will behave in the future. The likelihood of global climate change, with associated changes to carbon cycle processes on land and within the ocean, means, quite simply, that sink behavior cannot be expected to remain constant. Increasing political and economic attention to atmospheric pCO_2 levels will require scientists to provide convincing predictions, and assessments, of the variability in atmospheric pCO_2 and growth rates that we expect to occur. Prediction is the purview of modeling, which should be based on a sound scientific knowledge of processes; assessment can be performed with a combination of global measurement networks and related modeling approaches (e.g. data assimilation modeling, inverse modeling).

Inevitably, as we move beyond the era of global budgeting toward an increased focus on process-level understanding, we will also pay increasing attention to the regional and geographical distribution of carbon sources and sinks. The papers in this issue reflect this trend by focusing to a large extent on the regional behavior of the ocean. For example, the excess CO_2 detection techniques (see section 5) can reveal regions of the ocean where excess CO_2 accumulates preferentially [*Chen*, this issue]. Monitoring of such regions may be best suited for detection of changes in the rate of accumulation of excess CO_2 in the oceans. *Orr et al.* [this issue] use regional discrepancies between models, and between models and observations to identify specific processes and parameterizations that require improvement in models.

5. Excess CO_2 Signal Detection

It was recognized at least as early as 1964 that the increase of CO_2 in the ocean due to uptake of excess CO_2 was, in principle, directly measurable [e.g., *Postma*, 1964]. The basic principles required for such an approach were also understood at that time (e.g., correction of in situ DIC measurements for changes due to remineralization of soft tissue and dissolution of $CaCO_3$, comparison with "initial" or "preformed" concentrations at the sea surface). However, it was not until an extensive and reasonably high-quality data set for DIC and alkalinity was collected during the GEOSECS expedition, that the full potential of such an approach was recognized and formalized. *Brewer* [1978] and *Chen and Millero* [1979] independently published formal approaches to extracting the small excess (anthropogenic) component (order 40 μmol kg^{-1}) from the large and strongly varying natural background DIC concentration (order 2000 μmol kg^{-1}). They demonstrated the approach using data collected during the GEOSECS Atlantic Survey. As *Brewer* [1978] noted, "the oceanic CO_2 concentration is indeed increasing with time... this increase can be measured directly, and... the record of this increase is written in the interleaved structure of oceanic water masses."

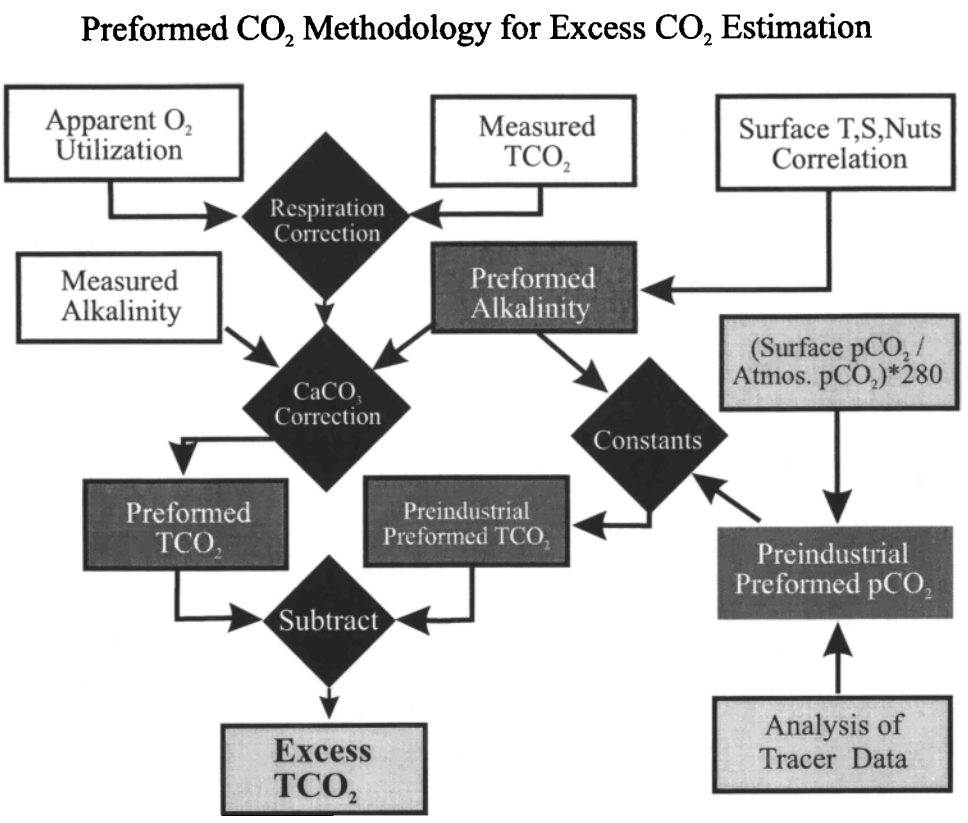

Figure 1. Flow-chart showing the basic steps used in the preformed CO_2 methods of excess CO_2 detection. Various researchers have taken different approaches to each of the steps shown here, particularly for the estimation of the preindustrial preformed pCO_2 or DIC concentration. However, all methods make use of variants of most of these basic steps either explicitly or implicitly. *Gruber et al.*'s [1996] approach to estimation of the preindustrial preformed DIC is considerably more sophisticated than the approach used in the Chen method for example, utilizing transient tracer-derived age data to estimate values of atmospheric pCO_2 at the time of water mass formation. Note that "constants" refers to the equilbrium constants that describe the solubility and speciation of CO_2 in seawater and "280" refers to the preindustrial atmospheric pCO_2. "Nuts" refers to nutrient data.

The signal detection methods introduced by *Brewer* [1978] and *Chen and Millero* [1979] differed in important details; however, they also shared a common conceptual background. I use the general term "preformed CO_2 method" to encompass this family of approaches, which all utilize a form of back calculation from concentrations measured within the ocean interior to quantities related to surface or so-called "preformed" concentrations. Conceptually, "preformed" concentrations refer to concentrations at water mass surface outcrops at the time of water mass formation (usually late winter), and in the case of DIC these have, of course, increased with time.

The underlying principle is to correct measured DIC concentrations for changes incurred since a water mass lost its ability to exchange gases directly with the atmosphere (see Figure 1) Inorganic carbon builds up naturally in subsurface waters due to oxidation of organic matter and dissolution of metal carbonates These effects can be diagnosed using the apparent oxygen utilization (AOU) and alkalinity deviations from the so-called "preformed alkalinity," respectively. If the preformed DIC level for the same water mass as it existed in the preindustrial era can be estimated, then the difference between the two calculated preformed values (present-preindustrial) gives the excess CO_2 content of the water mass. These basic steps are summarized in Figure 1. Obviously, significant problems arise in practice in accurately applying the required corrections and, particularly, in estimating the preindustrial preformed DIC values for different water masses [*Broecker et al.*, 1985]. *Sabine and Feely* [this issue] discuss such issues in some detail.

Following its introduction, the approach was applied extensively by Arthur Chen and coworkers to various oceanic regions culminating in a review [*Chen*, 1993] which included an estimate of the global ocean inventory of excess CO_2 for the year 1980 However, the approach also attracted some heavy criticism [e g , *Broecker et al.*, 1985]. The result was that, with the exception of Chen's continued work, the method fell out of use for almost 15 years and no further development and refinement of the basic approach took place in order to address the criticisms that had been leveled against it. During this period, indirect approaches to estimating anthropogenic CO_2 were pursued, notably model-based estimates "calibrated" with transient tracer distributions.

A major renaissance or rediscovery of this approach started in the mid-1990s owing to a combination of factors. For example, with the advent of global circulation modeling of excess CO_2 uptake, *Sarmiento et al* [1992] noted that the approach could be

useful for testing model predictions. *Wallace* [1995] in reviewing a variety of methods used to estimate ocean excess CO_2 inventories, noted that this approach "deserves renewed attention." Near simultaneously, *Gruber et al.* [1996] were working on refinements and clarifications to the approach [see *Sabine and Feely,* this issue]. Gruber's work led to the introduction of the so-called ΔC^* method, which represented a significant refinement of the earlier methods, including much improved approaches to the estimation of preindustrial preformed DIC levels for recently ventilated water masses (using transient tracer data), improved treatment of the effects of mixing of water masses, and detailed error assessments. As with the initial, post-GEOSECS introduction of these approaches, the prospect of an enormous high-quality data set for inorganic carbon, transient tracers and hydrography collected during WOCE and the associated JGOFS/WOCE Global CO_2 Survey [*Wallace*, 2001] may also have motivated the renaissance.

Sabine et al. [1999] applied the ΔC^* method to JGOFS/WOCE Global CO_2 Survey data collected in the Indian Ocean and compared the regional inventories of excess CO_2 with predictions made by a global carbon cycle GCM. *Chen* [this issue] notes that the overall inventories estimated by *Sabine et al.* [1999] are in fact not very different from those that he had previously estimated on the basis of earlier data [*Chen*, 1993], despite the use of the "refined" ΔC^* approach. His point is, clearly, that despite the extensive criticism leveled against such work in the past, the estimates that he made appear to be quite robust.

Sabine and Feely [this issue] look in detail at the differences between the method of *Chen and Millero* [1979] and Gruber's ΔC^* method. They do this by applying the *Chen and Millero* [1979] method to the JGOFS/WOCE Global CO_2 Survey data from the Indian Ocean and comparing the results with the ΔC^* estimates previously published by *Sabine et al.* [1999]. They agree with *Chen* [this issue] that the basin-wide inventories are almost identical using the two approaches but note also that there are substantial differences in the within-basin distributions. They argue that the ΔC^* approach gives the more reliable distributions.

Wanninkhof et al. [1999] also compared the ΔC^* approach with the Chen approach as well as with results from two carbon GCMs using a meridional section in the Atlantic between 62°N and 43°S. The inventories from all approaches also agreed closely (within 20%) when integrated throughout the Atlantic: however, once again, there were strong regional differences between the estimates based on the ΔC^* method with those calculated using the Chen method. A particularly strong difference was noted in the deep waters of the subtropical North Atlantic where the ΔC^* method appeared to give too low excess CO_2 levels in deep water. *Wanninkhof et al.* [1999] concluded that the deep penetration of excess CO_2 in this region was underestimated by the ΔC^* method. They also stated, for reasons not clearly presented, that the Chen approach gave levels that were too high in this region. *Wallace* [2001] similarly noted that excess CO_2 levels in deep waters of the South Atlantic may be underestimated using the ΔC^* method. This problem may be associated with the definition of the preindustrial preformed DIC values for waters that contain undetectable levels of chlorofluorocarbons (CFCs). *Gruber et al.* [1996] assumed that such waters are also uncontaminated with excess CO_2. However, ~30% of the excess CO_2 had already been released prior to around 1945 when CFCs first started to accumulate in the environment. *Wallace* [2001] noted that a large proportion of the CFC-free deep waters in the South Atlantic contain anthropogenic CCl_4 (a tracer with a significantly longer input history than the CFCs). These waters almost certainly contain excess CO_2. In many regions of the ocean (including the northern Indian Ocean addressed by *Sabine et al.* [1999]), the assumption that deep waters with undetectable CFC-levels are free of excess-CO_2 will be valid. However, in other regions, there will be significant "gray areas" where waters with undetectable levels of CFCs contain significant levels of excess CO_2. In such regions, the estimation of the preformed preindustrial DIC levels will continue to be a problem.

The data collected from the Indian Ocean during the CO_2 survey led *Goyet et al.* [1999] to introduce a significantly different approach to the estimation of excess CO_2. Their approach was to analyze the hydrographic and inorganic carbon data from the northern Indian Ocean using a multiparameter mixing analysis (an extension of an approach described by *Tomczak and Large* [1989]). This "MIX" approach [*Coatanoan et al.*, this issue] represents perhaps the most radical departure from the family of approaches initially introduced by *Brewer* [1978] and *Chen and Millero* [1979]. It appears to relax several assumptions inherent in the earlier techniques. However, the effect and appropriateness of some of the procedures, assumptions, and statistical weighting involved in the MIX approach as currently described are difficult to assess. The excess CO_2 distribution calculated using this technique showed large and significant differences with the estimates derived using the ΔC^* approach on the same data set [*Sabine et al.*, 1999]. These differences are discussed in some detail [*Coatanoan et al.*, this issue] although no firm conclusion is reached as to which approach is more accurate. It is fair to note that "Preformed CO_2 Methods", including the ΔC^* approach, have been subject to a long history of critical evaluation. The recently introduced MIX approach therefore warrants further critical assessment and refinement concerning its assumptions, underlying concepts, and implementation. The comparison between the two approaches presented in this issue is complicated by methodological inconsistencies in addition to the basic conceptual differences in approach (for example different stoichiometric coefficients were used to correct for respiration effects). In addition, the northern Indian Ocean might be considered a complex area (multiple water mass sources, unusual biogeochemistry) for such an initial comparison. A particularly useful diagnostic of the differences between the approaches appears to lie in the very different relationships between the excess CO_2 estimates and the CFC tracer concentrations [*Coatanoan et al.*, this issue].

Despite the uncertainties and differences of approach highlighted in this issue, it is also clear that the preformed CO_2 methods provide useful, spatially resolved, observation-based, and model-independent information concerning where and how much excess CO_2 has accumulated within the ocean. These preformed CO_2 methods estimate the total oceanic inventory of excess CO_2, i.e., all the extra carbon added since about 1750. However, this is not the only way in which oceanic excess CO_2 can be approached. The problem of defining preformed DIC levels and particularly the preindustrial, preformed DIC levels is likely to remain a fundamental problem in certain regions. The ΔC^* approach addressed this issue for well-ventilated water masses and very old waters, but as noted, there may also be regions with undetectable levels of CFCs where this remains a problem.

Recognition of this problem led *Wallace* [1995] to demonstrate that the temporal increase of excess CO_2 is also observable through the direct comparison of DIC data collected over decadal or longer intervals. Specifically, temporal changes in measured DIC that are not associated with analytical error or natural variability in other physical or biogeochemical factors (e.g., temperature, salinity, AOU, alkalinity) should reflect the build-up of excess CO_2. In any such comparison, natural varia-bility of such correlated parameters is likely to be encountered and has to be eliminated or corrected for before the excess CO_2 change can be estimated. Variants of this time series approach to excess CO_2 detection (see review by *Wallace*, 2001) have now been applied by *Sabine et al.* [1999], *Ono et al.* [1998], *Peng et al.* [1998], and *Slansky et al.* [1997]. It is likely that if the collection of high-quality inorganic carbon and hydrographic data sets from the oceans can be maintained, this approach will become more and more useful in constraining excess CO_2 uptake.

It is also important to remember that the locations where excess CO_2 accumulates are not necessarily the same as the locations where excess CO_2 crosses the air-sea interface, owing to the effects of transport by the ocean circulation [*Sarmiento et al.*, 1992]. The uptake of excess CO_2 from the atmosphere will be concentrated in regions where "old," poorly ventilated ocean waters regain close contact with the atmosphere (and where, in addition, gas-exchange is efficient in transferring CO_2 across the air-sea interface). These regions may, or may not, be coincident with regions of deep-water formation, which are regions where surface waters are transported back into the deep ocean again. The accumulation of excess CO_2 within the ocean will be largest in regions of the ocean, where recently ventilated surface waters converge. The excess CO_2 detection methods can therefore be used to investigate accumulation or storage; however, the process of uptake of excess CO_2 must generally be studied using models (see, however, *Holfort et al.* [1998] for an observation-based approach).

6. Three-Dimensional Modeling of Excess CO_2 Uptake and Carbon Transport

Until recently, most estimates of excess CO_2 storage in the oceans were also based on models of ocean uptake [e.g., *Sarmiento et al.*, 1992; *Siegenthaler and Joos*, 1992; *Stocker et al.*, 1994; *Caldeira and Duffy*, 2000]. Initially, various, very simple, vertically stacked box models were used (starting with *Oeschger et al.*, [1975]; see review by *Orr* [1993]), but over the past decade, ocean general circulation models have increasingly been employed. These GCMs separate the ocean into grids (resolution typically 0.5° to 4.5° latitudinal, 12-30 layers in the vertical) and are designed to simulate realistic aspects of the general circulation of the oceans and its thermal and haline structure. Mixing and convection in the models tend, however, to be highly parameterized. The models are "validated" against the distribution of ocean tracers such as natural and bomb-derived radiocarbon, CFCs, etc. The carbon cycle is represented in these models to varying degrees of complexity (see *Sarmiento et al.* [2000] for details).

Early work with GCMs [e.g., *Sarmiento et al.*, 1992] confirmed earlier box-model results [e.g., *Broecker et al.*, 1979] that the uptake of excess CO_2 is insensitive to the exact parameterization of air-sea gas exchange. This is consistent with the controlling factors for excess CO_2 uptake identified in section 2. Hence the skill of ocean models depends on their representation of surface water temperature and alkalinity distributions and their representation of vertical motions, particularly upward motions, within the ocean.

Most models have been adjusted to give a reasonable representation of surface temperatures, although the extent to which surface alkalinity is adequately represented is less clear. The issue of resolving vertical motions in the ocean is, however, nontrivial and is the reason for validation of such models through comparison with transient tracer uptake (e.g., bomb ^{14}C and more recently the CFCs). The tracers used for calibration are widely recognized as being imperfect analogs for excess CO_2 penetration particularly in their limited ability to assess the ventilation of water masses of intermediate "age" [*Wallace*, 1995; *Broecker*, 2001]. *Orr et al.* [this issue] therefore discuss the use of bomb-^{14}C as a validation tool in detail. However, it is worth noting that whereas we have several tracers for waters that sink downward into the ocean interior (e.g., bomb-radiocarbon, CFCs), we have few tools to address where older waters rise to the surface. In the context of a simple one-dimensional (1-D) model of the ocean, this distinction is not important. However for 3-D representations of the ocean, very large distances can separate the locations where waters rise to the surface, and take up excess CO_2, from the regions where they sink. The proximate physical forcing driving upwelling and sinking will also be different.

Orr [1993] noted the importance of judging how reliable model-based estimates of excess CO_2 uptake might be: "Unfortunately, we cannot yet adequately compare absorption of anthropogenic CO_2 in ocean models to that in the real ocean, but we can do the next best thing: compare models to one another." This was the approach used in assigning uncertainty to oceanic uptake estimates in the early 1990s. As noted above, since then, the methods to extract the excess CO_2 signal from oceanic DIC measurements have been rediscovered and undergone a renaissance, and the long-standing policy of "validating" models against tracer data continues. *Orr et al.* [this issue] reflect this by presenting model-model, model-tracer, and model-excess CO_2 comparisons, all addressing the problem of modeling excess CO_2 uptake by the oceans. These comparisons were made under the first phase of an international Ocean Carbon Model Intercomparison Project (OCMIP-1). The results point to several interesting agreements and differences between different GCMs and between the models and the observations. The differences reflect primarily the effects of varying model physics. Such model-model and model-data comparisons highlight the successes and deficiencies of models and, importantly, suggest issues and parameterizations that are in need of refinement. However, *Orr et al.* [this issue] also make the important point that bomb-^{14}C and excess CO_2, against which model predictions are compared, are also estimates rather than directly measurable quantities. They suggest that analysis of GCM output, in which the excess CO_2 content is accurately known, could be used to assess the uncertainties, errors, and optimal approaches underlying such estimates.

Sarmiento et al. [2000] presented results of a different set of OCMIP analyses, this time focused on the functioning of the natural, preindustrial ocean carbon cycle. This study used a set of ocean carbon GCMs to address the extent to which natural oceanic processes may have driven a net transport of carbon from

the Northern Hemisphere to the Southern Hemisphere. This issue is of considerable importance for the evaluation of present-day interhemispheric gradients of atmospheric CO_2 using atmospheric inverse modeling. Early studies by *Keeling and Heimann* [1986] and *Keeling et al.* [1989] inferred that during the preindustrial period, atmospheric pCO_2 was ~1 μatm lower in the Northern Hemisphere than in the Southern Hemisphere. This natural gradient is now reversed owing to fossil-fuel emissions, with the Northern Hemisphere pCO_2 now being ~3 μatm higher. Assuming that net terrestrial biosphere carbon storage was in steady state for the preindustrial era, a natural gradient must have been supported by either (1) an interhemispheric southward oceanic transport of ~1 Pg C yr^{-1} [*Keeling et al.*, 1989]; (2) effects of seasonal covariation of atmospheric CO_2 concentration and atmospheric circulation patterns that are not resolved by current measurements or atmospheric transport models (the seasonal rectifier of *Heimann et al.* [1986]; see also *Denning et al.* [1995]), or (3) a combination of both. Resolution of this issue is central to the interpretation of present-day meridional atmospheric pCO_2 gradients. Modelling of such gradients led to the inference that there is a large, Northern Hemisphere terrestrial carbon sink [e.g. *Tans et al.*, 1990]. *Fan et al.* [1999] have noted that a modern asymmetry between terrestrial biosphere sources and sinks (equatorial deforestation source coupled with a Northern Hemisphere terrestrial sink) complicates the inference through back-extrapolation [*Keeling et al.*, 1989] of preindustrial atmospheric pCO_2 gradients.

All such inferences are clearly sensitive to the assumed or modeled magnitude of the oceanic carbon transport [*Broecker and Peng*, 1992; *Holfort et al.*, 1998; *Wallace*, 2001] and/or the seasonal rectifier effect [*Law et al.*, 1996]. The paper by *Sarmiento et al.* [2000] therefore shows very clearly how detailed knowledge of the ocean can directly impact our understanding of sources and sinks on land. *Sarmiento et al.* [2000] used a model of ocean circulation to examine preindustrial carbon transports. The validity of the conclusions is of course conditional on the ability of the model to represent the important details of ocean circulation, including the spatial distribution of air-sea heat fluxes and heat transports, as well as biological processes (see critiques by *Watson et al.* [1995], *Stephens et al.* [1998], *Doney* [1999], *Murnane et al.* [1999]).

7. Implications and Recommendations

On the basis of the papers published in this issue together with *Sarmiento et al.* [2000], several general implications can be identified.

7.1. Excess CO_2 Detection

It is clear that although the signal of excess CO_2 can be extracted from measurements of DIC made within the contemporary ocean, the resulting estimates remain sensitive to the assumptions and specific methodological details employed. Even for methods that share a closely related conceptual background (e.g., the "Chen method" and the ΔC^* method), large regional differences in inferred concentrations can result. However, errors appear to cancel when the methods are applied over larger regions (e.g. basin scales) implying that basin scale estimates may in fact be quite robust. Some basic recommendations can be suggested: (1) Research should continue into the refinement and testing of excess CO_2 identification techniques. (2) Uncertainty in the stoichiometric coefficients that are required to back-calculate DIC to surface water conditions will always exist. Indeed the presence of excess CO_2 in the ocean complicates the estimation of such stoichiometric relationships from in situ data [*Wanninkhof et al.*, 1999]. This uncertainty should be explicitly incorporated into the overall uncertainty of excess CO_2 estimates, through application of a plausible range of stoichiometric coefficients. (3) Time series approaches to excess CO_2 signal detection are now possible but are conditional on the future collection of high-quality hydrographic and inorganic carbon data. (4) Carbon cycle model output should be analyzed in order to test and evaluate the various approaches to excess CO_2 identification [*Orr et al.*, this issue].

7.2. Modeling of Ocean Carbon Sources and Sinks

Model-model intercomparisons reveal significant differences in the regional uptake and accumulation of excess CO_2. Despite this, estimates of global excess CO_2 uptake to-date by the various models fall within a reasonably tight range [*Orr et al.*, this issue]. The model-model differences reflect, primarily, differences in model physics (although attention might also need to be focused on the representation of alkalinity). These differences are obviously important in limiting our regional understanding of excess CO_2 uptake and accumulation (for example in the critical Southern Ocean region). They may also affect our ability to predict future uptake, particularly in the event of climate-related changes to ocean circulation. The OCMIP-1 exercise made a major step forward in identifying such issues: the difficult but critical work will be to resolve them through model improvements. Continued comparisons with model-independent observations, including observations of physical fluxes such as heat transports, will guide such improvements.

In addition to characterizing sinks for excess CO_2, ocean models can also be used to "recreate" the preindustrial situation and, notably, to address the natural effect of oceanic carbon transport on atmospheric CO_2 distributions. Such information can guide the interpretation of atmospheric inversion modeling results concerning the distribution and magnitude of terrestrial carbon sinks. Once again the OCMIP exercise has pushed the field forward, and model results suggest that oceanic carbon transport is not large enough on its own to explain the postulated preindustrial atmospheric pCO_2 gradient (see *Fan et al.* [1999] for one possible explanation). However, the dependence of such transports on the representation of physical processes (vertical transport, convection, heat transport, the meridional overturning circulation, etc.), which are inherently difficult to model, requires continued critical evaluation [e.g., *Doney*, 1999; *Murnane et al.*, 1999; *Stephens et al.*, 1998; *Wallace*, 2001].

7.3. General

The take home message of this set of papers is that observation-based approaches to estimating excess CO_2 concentrations are of considerable utility but are sensitive to the details of the approach employed. On larger spatial scales, the effects of such differences may partially cancel, at least for methods that share a common conceptual framework. Similarly, with model-based estimates of excess CO_2 uptake and carbon transport, on the global scale, the level of agreement is encouraging, whereas on regional scales, significant discrepancies

exist. These regional and smaller scale discrepancies cannot be ignored because they reflect inadequacies in our representation of ocean biogeochemical and physical behavior. Such inadequacies will need to be addressed and resolved through continued research, including model-model and model-data comparisons. Critical assessment of excess CO_2 detection approaches using model-generated data sets should be attempted. The set of five papers discussed here combine to point a way forward. It is fair to say that the overall level of agreement between diverse approaches demonstrated here provides cause for optimism that we are developing the potential to monitor, understand, and maybe even predict the role of the ocean in future carbon uptake.

Acknowledgments. The author acknowledges valuable insight provided by Johannes Karstensen and support from the Deutsche Forschungsgemeinschaft (SFB-460).

References

Battle, M., M. Bender, P.P. Tans, J.W.C. White, J.T. Ellis, T. Conway, and R.J. Francey, Global carbon sinks and their variability, inferred from atmospheric O_2 and $\delta^{13}C$, *Science, 287*, 2467-2470, 2000.

Bender, M., T. Ellis, P. Tans, R. Francey, and D. Lowe, Variability in the O_2/N_2 ratio of southern hemisphere air, 1991-1994: Implications for the carbon cycle, *Global Biogeochemical Cycles, 10*, 9-21. 1996.

Brewer, P.G., Direct measurement of the oceanic CO_2 increase, *Geophys. Res. Lett., 5*, 997-1000, 1978.

Broecker, W.S., Carbon futures, in *Geosphere-Biosphere Interactions and Climate*, edited by L. Bengtsson and C.U. Hammer, Cambridge Univ. Press, New York, 2001.

Broecker, W.S., and T.H. Peng, Interhemispheric transport of carbon dioxide by ocean circulation, *Nature, 356*, 587-589, 1992.

Broecker, W.S., T. Takahashi, H.J. Simpson, and T.-H. Peng, Fate of fossil-fuel carbon dioxide and the global carbon budget. *Science, 206*, 409-418, 1979.

Broecker, W.S., T. Takahashi and T.-H. Peng, Reconstruction of past atmospheric CO_2 contents from the chemistry of the contemporary ocean, Rep. DOE/OR-857, 79 pp, U.S. Dep. Energy, Washington, DC, 1985.

Caldeira, K., and P.B. Duffy, The role of the Southern Ocean in uptake and storage of anthropogenic carbon dioxide, *Science, 287*, 620-622, 2000.

Chen, C.-T., The oceanic anthropogenic CO_2 sink, *Chemosphere, 27*, 1041-1064, 1993.

Chen, C.-T., Comments on "Anthropogenic CO_2 Inventory of the Indian Ocean" by C.L. Sabine et al., *Global Biogeochem. Cycles*, this issue.

Chen, C.-T., and F.J. Millero, Gradual increase of oceanic CO_2, *Nature, 277*, 205-206, 1979.

Ciais, P., P.P. Tans, J.W.C. White, M. Trolier, R.J. Francey, J.A. Berry, D.R. Randall, P.J. Sellers, J.G. Collatz, and D.S. Schimel, Partitioning of ocean and land uptake of CO_2 as inferred by $\delta^{13}C$ measurements from the NOAA Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network. *J. Geophys. Res., 100*, 5051-5070, 1995.

Coatanoan, C., C. Goyet, N. Gruber, C.L. Sabine and M. Warner, Comparison of two approaches to quantify anthropogenic CO_2 in the ocean: results from the northern Indian Ocean, *Global Biogeochem. Cycles*, this issue.

Denning, A.S., I.Y. Fung, and D. Randall, Latitudinal gradient of atmospheric CO_2 due to seasonal exchange with land biota, *Nature, 376*, 240-243, 1995.

Doney, S.C., Major challenges confronting marine biogeochemical modeling, *Global Biogeochem. Cycles, 13*, 705-714, 1999.

Enting, I.G., C.M. Trudinger, and R.J. Francey, A synthesis inversion of the concentration and $\delta^{13}C$ of atmospheric CO_2, *Tellus Ser. B, 47*, 35-52, 1995.

Fan, S., M. Gloor, and J. Mahlman, A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models, *Science, 282*, 442-446, 1998.

Fan, S.M., T.L. Blaine, and J.L. Sarmiento, Terrestrial carbon sink in the Northern Hemisphere estimated from the atmospheric CO_2 difference between Mauna Loa and the South Pole since 1959, *Tellus Ser. B, 51*, 863-870, 1999.

Francey, R.J., P.P. Tans, and C.E. Allison, Changes in oceanic and terrestrial carbon uptake since 1982, *Nature, 373*, 326-330, 1995.

Goyet, C., C. Coatanoan, G. Eischeid, T. Amaoka, K. Okuda, R. Healy, and S. Tsunogai, Spatial variation of total CO_2 and total alkalinity in the northern Indian Ocean: A novel approach for the quantification of anthropogenic CO_2 in seawater, *J. Mar. Res., 57*, 135-163, 1999.

Gruber, N., J.L. Sarmiento, and T.F. Stocker, An improved method for detecting anthropogenic CO_2 in the oceans, *Global Biogeochem. Cycles, 10*, 809-837, 1996.

Heimann, M., C.D. Keeling, and I.Y. Fung, Simulating the atmospheric carbon dioxide distribution with a three dimensional tracer model, in *The Changing Carbon Cycle: A Global Analysis*, edited by J.R. Trabalka and D. E. Reichle, pp. 17-48, Springer-Verlag, New York, 1986.

Holfort, J., K.M. Johnson, B. Schneider, G. Siedler, and D.W.R. Wallace, Meridional transport of dissolved inorganic carbon in the South Atlantic Ocean, *Global Biogeochem. Cycles, 12*, 479-499, 1998.

Indermuehle, A., et al., Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica, *Nature, 398*, 121-126, 1999.

Keeling, C.D., and M. Heimann, Meridional eddy diffusion model of the transport of atmospheric carbon dioxide, 2, Mean annual carbon cycle, *J. Geophys. Res., 91*, 7782-7796, 1986.

Keeling, C.D., R.B. Bacastow, A.L. Carter, S.C. Piper, T.P. Whorf, M. Heimann, W.G. Mook, and H. Roeloffzen, A three dimensional model of atmospheric CO_2 transport based on observed winds, 1, Analysis of observational data, in *Aspects of Climate Variability in the Pacific and the Western Americas, Geophys. Monogr. Ser.*, vol. 55, pp. 165-236, edited by D.H. Peterson, AGU, Washington, DC, 1989.

Keeling, C.D., T.P. Whorf, M. Wahlen, and J. Vanderplicht, Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980, *Nature, 375*, 666-670, 1995.

Keeling, R.F., R.P. Najjar, and M.L. Bender, What atmospheric oxygen measurements can tell us about the global carbon-cycle, *Global Biogeochem. Cycles, 7*, 37-67, 1993.

Keeling, R.F., S.C. Piper, and M. Heimann, Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration, *Nature, 381*, 218-221, 1996.

Langenfelds, R.L., R.J. Francey, and L.P. Steele, Partitioning of the global fossil CO_2 sink using a 19-year trend in atmospheric O_2, *Geophys. Res. Lett., 26*, 1897-1900, 1999.

Law, R.M., et al., Variations in modeled atmospheric transport of carbon dioxide and the consequences for CO_2 inversions, *Global Biogeochem. Cycles, 10*, 783-796, 1996.

Lee, K., R. Wanninkhof, T. Takahashi, S.C. Doney and R. Feely, Low interannual variability in recent oceanic uptake of atmospheric carbon dioxide, *Nature, 396*, 155-159, 1998.

Maier-Reimer, E., and K. Hasselmann, Transport and storage of CO_2 in the ocean: An inorganic ocean-circulation carbon cycle model, *Clim. Dyn., 2*, 63-90, 1987.

Murnane, R.J., J.L. Sarmiento, and C. Le Quéré, Spatial distribution of air-sea CO_2 fluxes and the interhemispheric transport of carbon by the oceans, *Global Biogeochem. Cycles, 13*, 287-305, 1999.

Oeschger, H., U. Siegenthaler, U. Schotterer, and A. Gugelmann, A box-diffusion model to study the carbon dioxide exchange in nature, *Tellus, 27*, 168-192, 1975.

Ono, T., S. Watanabe, K. Okuda, and M. Fukasawa, Distribution of total carbonate and related properties in the North Pacific along 30°N. *J. Geophys. Res., 103*, 30,873-30,883, 1998.

Orr, J.C., et al., Estimates of anthropogenic carbon uptake from four three-dimensional global ocean models, *Global Biogeochem. Cycles*, this issue.

Orr, J.C., Accord between ocean models predicting uptake of anthropogenic CO_2, *Water Air Soil Pollut., 70*, 465-481, 1993.

Pearman, G.I., and P. Hyson, The annual variation of atmospheric CO_2 concentration observed in the Northern Hemisphere, *J. Geophys. Res., 86*, 9839-9843, 1981.

Peng, T.-H., R. Wanninkhof, J.L. Bullister, R.A. Feely, and T. Takahashi, Quantification of decadal anthropogenic CO_2 uptake in the ocean based on dissolved inorganic carbon measurements, *Nature, 396*, 560-563, 1998.

Postma, H., The exchange of oxygen and carbon dioxide between the ocean and the atmosphere, *Neth. J. Sea Res., 2*, 258-283, 1964.

Quay, P.D., B. Tilbrook, and C.S. Wong, Oceanic uptake of fossil fuel CO_2: Carbon-13 evidence. *Science, 256*, 74-79, 1992.

Rayner, P.J., I.G. Enting, R.J. Francey, and R. Langenfelds, Reconstructing the recent carbon cycle from atmospheric CO_2, $\delta^{13}C$ and O_2/N_2 observations. *Tellus Ser. B, 51*, 213-232, 1999.

Sabine, C.L., and R.A. Feely, Comparison of recent Indian Ocean anthropogenic CO_2 estimates with a historical approach, *Global Biogeochem. Cycles*, this issue.

Sabine, C.L., R.M. Key, K.M. Johnson, F.J. Millero, A. Poisson, J.L. Sarmiento, D.W.R. Wallace, and C.D. Winn, Anthropogenic CO_2 inventory of the Indian Ocean, *Global Biogeochem. Cycles, 13*, 179-198, 1999.

Sarmiento, J.L., J.C. Orr, and U. Siegenthaler, A perturbation simulation of CO_2 uptake in an ocean general circulation model, *J. Geophys. Res., 97*, 3621-3645, 1992.

Sarmiento, J.L., P. Monfray, E. Maier-Reimer, O. Aumont, R.J. Murnane, and J.C. Orr, Sea-air CO_2 fluxes and carbon transport: A comparison of three ocean general circulation models, *Global Biogeochem. Cycles, 14*, 1267-1282, 2000.

Schimel, D., I.G. Enting, M. Heimann, T.M.L. Wigley, D. Raynaud, D. Alves, and U. Siegenthaler, CO_2 and the carbon cycle, in *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios* edited by J.T. Houghton, et al., pp. 35-71, Cambridge University Press, New York, 1995.

Siegenthaler, U., and F. Joos, Use of a simple-model for studying oceanic tracer distributions and the global carbon-cycle, *Tellus Ser. B, 44*, 186-207, 1992.

Siegenthaler, U., and J.L. Sarmiento, Atmospheric carbon dioxide and the ocean, *Nature, 365*, 119-125, 1993.

Slansky, C.M., R.A. Feely, and R. Wanninkhof, The stepwise linear regression method for calculating anthropogenic CO_2 invasion into the north Pacific Ocean, in *Biogeochemical Processes in the North Pacific*, edited by S. Tsunogai, pp. 70–79, Japan Marine Science Foundation, Tokyo, Japan, 1997.

Smith, H.J., H. Fischer, M. Wahlen, D. Mastroianni, and B. Deck, Dual modes of the carbon cycle since the Last Glacial Maximum, *Nature, 400*, 248-250, 1999.

Stephens, B.B., R.F. Keeling, and M. Heimann, Testing global ocean carbon cycle models using measurements of atmospheric O_2 and CO_2 concentration, *Global Biogeochem. Cycles, 12*, 213-230, 1998.

Stocker, T.F., W.S. Broecker, and D.G. Wright, Carbon uptake experiments with a zonally-averaged ocean circulation model, *Tellus Ser. B, 46*, 103-122, 1994.

Takahashi, T., R. A. Feely, R. Weiss, R. Wanninkhof, D. W. Chipman, S. C. Sutherland, and T. T. Takahashi, Global air-sea flux of CO_2: An estimate based on measurements of sea-air pCO_2 difference, in *NAS Colloquium Volume on Carbon Dioxide and Climate Change*, edited by C.D. Keeling, *Proc. Natl. Acad. Sci. USA, 94*, 8292-8299, 1997.

Takahashi, T., R. H. Wanninkhof, R. A. Feely, R. F. Weiss, D. W. Chipman, N. Bates, J. Olafson, C. Sabine, and S.C. Sutherland, Net sea-air CO_2 flux over the global oceans: An improved estimate based on the sea-air pCO_2 difference, in *Proceedings of the 2nd International Symposium CO_2 in the Oceans*, edited by Y. Nojiri, pp. 9-15, Cent. for Global Environ. Res., Nat. Inst. for Environ. Stud., Tsukuba, Japan, 1999.

Tans, P.P., and D.W.R. Wallace, Carbon cycle research after Kyoto, *Tellus Ser. B, 51*, 562-571, 1999.

Tans, P.P., I.Y. Fung, and T. Takahashi, Observational constraints on the global atmospheric CO_2 budget, *Science, 247*, 1431-1438, 1990.

Tomczak, M., and D.G.B. Large, Optimum multiparameter analysis of mixing in the thermocline of the Eastern Indian Ocean, *J. Geophys. Res., 94*, 16,141-16,149, 1989.

Wallace, D.W.R., Monitoring global ocean carbon inventories, *Ocean Observing Syst. Dev. Panel Background Rep. 5*, 54 pp., Texas A&M Univ., College Station, Tex., 1995.

Wallace, D.W.R., Storage and Transport of Excess CO_2 in the Oceans: The JGOFS/WOCE Global CO_2 Survey, in *Ocean Circulation and Climate*, edited by J. Church, G. Siedler, and J. Gould, Academic Press, San Diego, Calif., 2001.

Wanninkhof, R., S.C. Doney, T.-H. Peng, J.L. Bullister, K. Lee, and R. A. Feely, Comparison of methods to determine the anthropogenic CO_2 invasion into the Atlantic Ocean, *Tellus Ser. B, 51*, 511-530, 1999.

Watson, A.J., P.D. Nightingale, and D.J. Cooper, Modeling atmosphere ocean CO_2 transfer, *Phil. Trans. Royal Soc. London Ser. B, 348*, 125-132, 1995.

D.W.R. Wallace, Forschungsbereich Marine Biogeochemie, Institut für Meereskunde an der Universität Kiel, Düsternbrooker Weg 20, 24105 Kiel, Germany. (dwallace@ifm.uni-kiel.de)

(Received October 6, 2000; revised January 5, 2001;
accepted January 12, 2001)